Natural Occurrence and Synthesis of Two New Post-Spinel Polymorphs of Chromite

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Chromite is a common accessory mineral occurring in most meteorites and in many mantle rocks. A high-pressure polymorph of chromite, the first natural sample with the calcium ferrite structure, has been discovered in the shock veins of the Suizhou meteorite. Synchrotron x-ray diffraction analyses reveal the sample has an orthorhombic $CaFe_2O_4$-type (CF) structure. The unit-cell parameters are a = 8.954(7) Å, b = 2.986(2) Å, c = 9.891(7) Å, and V (volume) = 264.5(4) Å^3 (Z, the number of molecules per unit cell, = 4), with space group Pnma. The new phase has a density of 5.62 g/cm^3, which is 9.4 % denser than the chromite-spinel phase. Laser-heated diamond anvil cell experiments were performed to establish that chromite-spinel transforms to CF at 12.5 GPa and then to the recently-discovered $CaTi_2O_4$-type (CT) structure above 20 GPa. With the ubiquitous presence of chromite, the CF and CT phases may be among the more important index minerals for tracking the natural transition sequence and P-T conditions in mantle rocks, shock-metamorphosed terrestrial rocks, and meteorites.

Chromite is a common accessory mineral that is a member of the spinel group of minerals, a group of oxides that have very similar structures. Chromite occurs in most meteorites and in many mantle rocks. The experimentally calibrated CF and CT polymorphs of chromite could therefore be ideal pressure gauges, not only for shock-metamorphosed terrestrial rocks and meteorites, but also for mantle rocks covering the important pressure range throughout the transition zone.

Spinel structure is the most important type of structure occurring in minerals in Earth's mantle. $CaFe_2O_4$-type (CF) and $CaTi_2O_4$-type (CT) structures were proposed as the top candidates for "post-spinel" transitions in the deep mantle (**Figure 1**). However, no dense post-spinel polymorphs have been discovered in nature. A preliminary examination of the shock-metamorphosed Suizhou meteorite has recently revealed a CT polymorph of chromite $(Fe,Mg)(Cr,Al)_2O_4$. This study reports another new CF-type polymorph of chromite in the same meteorite.

Synthesis experiments were performed at pressures from 7.5 to 25 GPa at a temperature of 2000°C, using laser-heated diamond anvil cells. Our experiments indicate that chromite-spinel transforms to the CF structure above 12.5 GPa, and to the CT structure above 20 GPa (**Figure 2**). The x-ray diffraction pattern of the quenched CF polymorph was indexed to give lattice parameters a = 8.955(7)Å, b = 2.985(2)Å, c = 9.909(7)Å, V = 264.9(4)Å^3 (Z=4), density (ρ) = 5.61 g/cm^3, and space group *Pnma*. For the CT polymorph, the parameters are a = 9.467(5) Å, b = 9.550(7) Å, c = 2.905(2) Å, V = 262.6(4) Å^3 (Z=4), ρ = 5.65g/cm^3, and space group *Cmcm*. The densities of synthetic CF and

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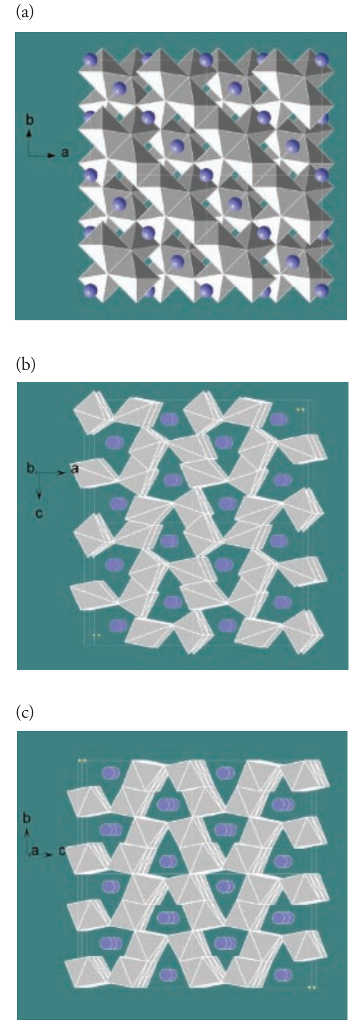
CT polymorphs are 9.4 % and 10.1 % denser, respectively, than that of chromite.

Some chromite grains in the Suizhou meteorite covered a shock-induced pressure gradient. These grains show three zones of distinct densities corresponding to the pressure gradient - a CT phase zone close to the shock vein, a chromite zone relatively apart from the vein, and a lamella-rich (layered) zone between the CT phase zone and the chromite zone (**Figure 3**). These three zones have a uniform chromite chemical composition. We used a synchrotron x-ray beam to probe the shock chromite grain *in situ* in the thin section mount of the meteorite, and confirmed that a zone in contact with the shock vein, ranging from 20 to 30 μm in width, had transformed into a fine-grained polycrystalline aggregate with a CT-type structure identical to the CT phase that was synthesized experimentally. We also confirmed that the clear zone at the low-pressure end has the usual chromite-spinel structure.

We focused the x-ray microprobe on the lamella-like zone between the CT and spinel zones and obtained distinct diffraction patterns for the CT phase, which are consistent with a mixture of the CF and spinel phases, and a trace amount of the CT phase, with the fraction of spinel decreasing toward the shocked vein and the CT phase increasing toward the shocked vein. The x-ray patterns collected from different orientations of the sample show that the lamellae-like slices are polycrystalline in nature. X-ray reflections from the CF phase were indexed to an orthorhombic cell with parameters a = 8.954(7) Å, b = 2.986(2) Å, c = 9.891(7) Å, and V = 264.5(4) Å^3 (Z=4). The structure is identical to the synthetic CF phase in our high-pressure experiment. The calculated density of the natural CF phase is ρ = 5.62 g/cm^3, which is 9.4 % denser than that of the chromite-spinel phase. This is the first natural occurrence of a dense $FeCr_2O_4$ polymorph displaying the CF structure.



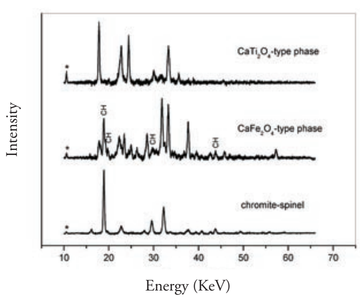


Figure 2. X-ray diffraction patterns from the natural chromite-spinel, synthesized $CaFe_2O_4$-type, and $CaTi_2O_4$-type phases. The peaks labeled with 'CH' from the residue of the starting material, chromite-spinel. * = escape peaks.

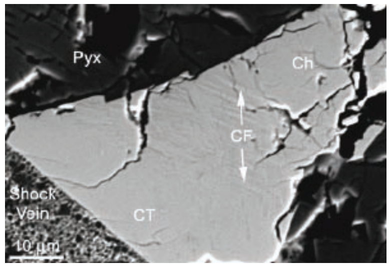


Figure 3. Back-scattered electron images (BSE) of shock-metamorphosed chromite-spinel grains in the Suizhou meteorite. A chromite grain was transformed to a $CaTi_2O_4$-type phase zone (CT) contacting with the shock vein, and partially to a $CaFe_2O_4$-type phase zone (CF) between the CT phase zone and the chromite zone (Ch) apart from the shock vein. The CF phase occurs as lamella-like slices associating with a chromite matrix, and two to three sets of slices are observed. On the image, both the CT and CF phases are brighter than chromite. Pyx = pyroxene.

Figure 1. Schematic view of the (A) spinel, (B) $CaFe_2O_4$, and (C) $CaTi_2O_4$ type structures. The spinel structure has octahedral and tetrahedral sites. In the CF and CT structures, a compact three-dimensional network is formed by edge- and corner-sharing octahedra, with hollow channels parallel to the b axis (CF structure) and the a axis (CT structure), respectively, where the large Ca cations are located. These two structures contain dodecahedral and octahedral sites; the difference between the two structures lies in slight modifications of the polyhedral linkage. There are two types of FeO_6 octahedral sites in the CF structure, and one type of FeO_6 octahedral site in the CT structure.